Investigating Longevity of Corrosion Inhibitors and Performance of Deicer Products Under Storage or After Pavement Application

Executive Summary

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Prior to this research, little was known about how long the corrosion inhibitors and the deicer products remain effective during storage and on the pavement once applied during the winter storm. The direct cost of inhibited chemicals can be much higher than that of the non-inhibited chemicals. As such, this study aimed to evaluate the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under various storage conditions or after pavement application.

Multiple established analytical methods were used to monitor the temporal evolution of the identified deicer properties under field storage, by randomly sampling the solid or liquid deicers periodically and analyzing them in the laboratory. For deicer characterization, the differential scanning calorimetry (DSC) thermogram can provide information on the characteristic temperature (Tc) and the heat flow (H) during the liquid/solid phase transition of a given deicer, which also shed light on a more realistic working temperature range than a deicer's eutectic temperature. Specifically, the first peak temperature at the high temperature end of the warming cycle is defined as the Tc of the deicer, which corresponds to the temperature below which ice crystals start to form in the aqueous phase. The H for a deicer solution indicates the amount of thermal energy needed for the liquid/solid phase transition. Conceptually, the stronger a deicer, the lower the Tc and the smaller the H associated with the Tc peak. A strong correlation between the DSC data (Tc and H) and the Modified SHRP Ice Melting test data has been developed. This provides another opportunity to utilize the DSC test results, that is, to predict the ice melting capacity (IMC) of a chloride-based deicer.

• Three liquid deicers (MgCl2-based FreezGard, Calcium Chloride with Boost - CCB, and NaCl+GLT) and one solid deicer (NaCl-based IceSlicer) were selected for the field storage monitoring (see Table above) and the key properties tested include the chloride and inhibitor concentrations, corrosion parameters (Ecorr and PCR), pH, electrical conductivity, and performance parameters (Tc and IMC30ºF, 60min). None of liquid deicers lost their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). The NaCl-based solid deicer did not lose its quality over the 12 months of field storage, regardless of the storage condition (covered or uncovered). For all four deicers, the observed fluctuations in their properties seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage. During the 14-month field monitoring, NaCl+GLT was the only liquid deicer to have non-passing corrosion scores, suggesting potential shelf-life issues.

• From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer. For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage monitoring period.

• The GLT inhibitor used alone or as additive to the NaCl-based deicer showed no benefit in suppressing effective temperature or in providing ice melting capacity. The inhibitor packages used in the CCB and FreezGard deicers slightly increased the effective temperature of their respective brine and showed little effect on the ice melting capacity (based on the DSC data).

However, different from GLT, these inhibitor packages showed some limited ice melting capacity when used alone. In a word, while these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.

• With few exceptions, the IceSlicer samples from the covered pile generally featured slightly higher chloride concentrations and significantly lower inhibitor concentrations, relative to those from the uncovered pile. While the chloride concentration in both covered and uncovered piles remained relatively consistent over the 12 months of field storage, the inhibitor concentration in both piles tended to increase over time. The deicer corrosivity to steel (PCR) fluctuated between 60 and 100, regardless of the storage condition or the sieving of the deicer sample, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The inhibitor-to-chloride concentration ratio in the cistern attached to the uncovered pile remained fairly consistent in the first eight months of monitoring. Yet the low inhibitor concentrations in the cistern during last four months may be correlated with the high inhibitor concentrations in the uncovered pile, both suggesting that

the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.

• ANN has demonstrated great potential in finding meaningful, logical results from the noisy data associated with the metallic corrosion experiments. One ANN model was established to correlate the corrosion data from the electrochemical test method with those from the PNS/NACE test method (featuring a R-square of 0.84). Two additional ANN models were established to achieve better understanding of the complex correlation between the deicer composition (deicer type, chloride and inhibitor concentrations, pH, and electrical conductivity) and the deicer corrosivity (in PCR) and performance (in Tc) respectively. According to the ANN modeling, there are strong correlations inherent in the deicer samples (indicated by the R-square values of 0.91 and 0.98 for PCR and Tc respectively), whereas the trends differ as a function of the deicer type.

• High Ecorr values generally corresponded with low corrosivity (PCR) values. The Ecorr value higher than -562 mV (vs. SCE) generally corresponded to PCR values lower than 30, which is desirable per the guidelines by the Pacific Northwest Snowfighters Association. It should be noted, however, that an Ecorr value lower than -562 mVSCE does not necessarily indicate a PCR value higher than 30. As such, the electrochemical test could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.

This study also investigated the longevity of corrosion inhibitors and the performance of three corrosion-inhibited deicer products (see Table above), by daily sampling of deicer residuals on the pavement for seven days after deicer application for a black ice event, a man-made snow event, and a natural snow event respectively. To simulate realistic climatic and logistical situations, the field operational tests were conducted at the TRANSEND facility at Lewistown, MT (the target and actual conditions for the three events are shown in the Table below). Subsequently, the analytical methods established previously were used to analyze the properties of pavement-collected samples in the laboratory.

• In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.

• The samples collected from the control test lanes (with no deicer applied) seemed to contain contaminants that affect their UV-vis spectrum, pH, and corrosion data, yet their low chloride concentration and low conductivity suggested the absence of salt. The Ecorr data of steel in control samples suggest that the natural snow event and the black ice event collected the least and the most amount of contaminants from pavement respectively, while the man-made snow event fell in between.

• Out of the seven test days for the three events, NaCl+GLT had the greatest number of passing PCR values (14/21), followed by CCB (13/21) and FreezGard (11/21).

• A number of mechanisms may have accounted for the much lower chloride recovery from the pavement during the natural snow event, relative to the man-made snow event, including warmer pavement temperature, more precipitation, loss of deicer to the leveling-off step, and more time waited before day-one sampling.

• The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitors differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.

• The black ice event featured a total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7. The percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Starting on day 5, the chloride recovery for all three deicers significantly dropped, attributable to the rain precipitation on day 3 and the snow precipitation on day 3 (trace amount), day 4 (>1/2″), and day 5 (1/2″). Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. The PCR of residuals recovered from the pavement by day 4 was approximately 40, 15 and 35 for NaCl+GLT, CCB, and FreezGard respectively. Note that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory

, where the PCR was 32, 21, and 16 for NaCl+GLT, CCB, and FreezGard respectively.

• The man-made snow event featured 1″ of artificial snow and a total of 0.26″ of natural snow during day 3 and day 4. The percent of chloride recovered from the pavement by day 7 was approximately 20%, 16%, and 8% for NaCl+GLT, CCB, and FreezGard respectively. Up to 38% and 26% of the inhibitors were recovered from the pavement seven days after the application of NaCl+GLT and CCB respectively. The PCR of residuals recovered from the pavement by day 7 was approximately 51, 72 and 31 for NaCl+GLT, CCB, and FreezGard respectively. The un-diluted samples collected from the deicer test lanes during the man-made snow event featured the greatest number of non-passing PCR values. This could be partly attributed to the generally low inhibitor concentrations that remained on the pavement, coupled with the relatively high chloride concentrations that remained on the pavement. The PCR values showed no clear relationship with storm type, deicer type or sampling time.

• The natural snow event featured 3.5-4″ of natural snow in the first 24 hours and about 0.75″ of blowing snow on day 2. The percent of chloride recovered from the pavement was less than 0.7% by day 6 and less than 0.5% by day 7, for all three deicers. Up to 21% and 4% of the GLT inhibitor was recovered from the pavement one day and five days after the deicer application respectively. Up to 83% of the FreezGard inhibitor was recovered from the pavement seven days after the deicer application. Such unusually high inhibitor recovery efficiencies for the natural snow event present a significant contrast to the extremely low chloride recovery.

The PCR of residuals recovered from the pavement by day 1 was approximately 7, 10 and 18 for NaCl+GLT, CCB, and FreezGard respectively. The un-diluted samples collected from the deicer test lanes during the natural snow event featured the lowest PCR values, all of which remained below the PNS-specified 30%. This could be attributed to the extremely low chloride concentrations that remained on the pavement. The PCR values showed no clear relationship with storm type or deicer type.

In summary, the five objectives of this research were achieved to various degrees by this work as follows.

• The longevity of the corrosion inhibitors and the duration in which they persist with the deicer (both under storage and after pavement application): - achieved. No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage. During the 14-month field monitoring, NaCl+GLT was the only liquid deicer to have non-passing corrosion scores, suggesting potential shelf-life issues. The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitors differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.

• The possible effects of temperature, UV intensity, exposure, and dilution on inhibitors in common chloride deicers and deicer performance: - mostly achieved. From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer.

• The cost-effectiveness of including inhibitors in deicers: - partially achieved. This research suggests that the inhibitors did not provide side benefits in deicer performance, which should be considered during the collaborative decision-making for materials selection.

• Any inhibitor effect on freezing point suppression or deicer effectiveness: - achieved. While these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.

• The most effective deicer for different winter weather scenarios: - achieved. In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.

Implementation Recommendations

• The three liquid deicers ($MgCl_2$-based FreezGard, $CaCl_2$-based CCB, and NaCl+GLT) investigated did not lose their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). As such, it is unnecessary to implement any mixing for the liquid deicer tanks during storage. However, it is important to do so immediately prior to the use of the liquid deicers, to ensure uniform composition and minimize stratification.

• It would be best to cover solid deicers during field storage to minimize leaching of active ingredients (especially corrosion inhibitor), but the solid deicer after 12 months storage under uncovered conditions can still be an effective deicer despite its reduced corrosion inhibition.

• When determining whether the inclusion of corrosion inhibitor in deicers is economical, be aware that the investigated inhibitor packages did not show any side benefits in deicer performance and they served merely as corrosion inhibitors for the deicer products. The fate and transport of inhibitors differed from those of chlorides, once applied on the pavement.

• Without dilution by rain or snow precipitation (e.g., the early days of black ice event), the percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. While such residuals could be washed away by precipitation, their presence on the pavement could potentially be measured and taken into consideration when re-applying chemicals for snow and ice control.

• This project revealed that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory. It merits further investigation to develop laboratory tests that can correlate better with the actual field corrosion of metals caused by deicer exposure, taking the fate and transport of corrosion inhibitors (vs. chlorides), relative humidity, temperature cycles, etc. in the service environment into account.